CORRELATION BETWEEN CARBON RESIDUE AND MOLECULAR WEIGHT

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INTRODUCTION

Petroleum residua are materials obtained by nondestructive distillation of petroleum, usually below 350°C (660°F) since thermal decomposition can be substantial above this temperature (1). Distillation can be at atmospheric pressure (atmospheric residuum) or reduced pressure (vacuum residuum). Residua are usually tacky (atmospheric) or hard (vacuum) at room temperature. These materials typically have low atomic hydrogen-to-carbon ratios, which require hydrogen addition or carbon rejection (coking) schemes to convert them to liquid fuels. They can be difficult to process because of relatively high concentrations of elements other than carbon and hydrogen, and high viscosities (1).

Simple physical property measurements were once considered adequate to predict feedstock behavior in petroleum refining (1,2). The use of various types of residua available worldwide with different properties has added complexity to these considerations (3). Residua composition and properties must be understood to optimize refining strategies (4). Measurements such as elemental analysis, metals content, asphaltene content, and carbon residue provide some indication of residua behavior, but are not single predictors for upgrading processes (5). More insight is needed about the components of residua that cause specific problems in processing (6). The possibility exists that data from various analyses can be combined in a manner to provide insight into behavior during refining (7).

Molecular weight and molecular size are the most misunderstood parameters of petroleum constituents. There are many reports of high molecular weights (100,000-300,000 Daltons) for asphaltenes (8). True molecular weights for asphaltenes very rarely exceed 3,000. Apparent higher values are due to molecular association effects due to the presence of polar constituents causing inter- and intramolecular interactions.

EXPERIMENTAL

The samples were vacuum residua and commercial grade asphalt materials from various sources. Asphaltenes were determined by adding n-heptane at a 40:1 volume ratio (9). Microcarbon residue (MCR) values were determined according to ASTM D-4530. This requires less than 1 g of sample and correlates with the Conradson carbon residue (CCR) test, which consumes 5-10 g sample (10). Number average molecular weights were determined by ASTM D-2503 using a Knaur vapor pressure osmometer (VPO) in toluene at 140°F (60°C). Although pyridine would be considered more desirable for breaking up molecular associations between more polar materials, toluene was used in this study since complete solubility could not be achieved in pyridine for residua asphaltenes.

RESULTS AND DISCUSSION

Ideally, a predictive model can be applied to various feedstocks from different sources and of different types such as waxy, resinous, etc. to predict MCR or CCR values, which are predictors of coke yield. Carbon residue values are related to phase separation and delayed coking tendencies in a refinery (1,7,11). Asphaltene content can be used to provide a rough correlation with carbon residue values (12). For the twelve residua considered in the current study, the correlation between percent asphaltenes and MCR yields a correlation coefficient (r) value of only 0.584. Additional refinement is needed to be a useful predictor of residue formation tendencies. This refinement involves including association effects. Residua with relatively low heteroatom contents yield MCR values significantly lower thanresidua with relatively higher heteroatom contents (13).

A correlation relating asphaltene content, molecular weight and heteroatom content with CCR and MCR of whole residua has been developed (14). Subsequent results suggest that the inclusion of heteroatoms is not necessary, since heteroatom associative affects are already taken into account by measuring the apparent molecular weights of the asphaltenes. In the previous study, the intercept was 8.19 wt.% MCR, which is due to contributions from other aromatic and polar materials in the residua.

The fractional contributions of the various constituents of residua to MCR have been shown to be additive (13). Thus, by considering the contribution of all the fractions, a more universal correlation can be obtained. A new correlation with MCR values and apparent molecular weights in toluene is shown in Figure 1. This consists of twelve residua, six asphaltenes and twelve chromatographic fractions (six aromatics and six polars) considered as whole materials, and the six asphaltenes and the twelve chromatographic fractions considered as fractional contributions

(13,15) Saturate fractions containing no significant aromatic structures and providing no contribution to MCR are not included. The correlation coefficient is 0.943 for 44 points, with a slope of 0.0198 and an intercept of -0.42. This is within experimental error of 0 wt.% MCR. These results suggest a generic universality for residua constituents between molecular weights and residue forming tendencies.

In Figure 1, two asphaltenes fall near the line, while four do not. The four that do not exhibit unrealistically high molecular weights relative to their MCR values. These latter four were not included in the linear equation. The high molecular weights are most likely due to severe associations of these very polar materials in toluene. The two asphaltenes which fell near the line have heteroatom content (N+O+S) of less than 6 wt.%, while the four that are far to the right of the line have heteroatom contents greater than 6 wt.%. The high heteroatom content contributes to polarity and association effects.
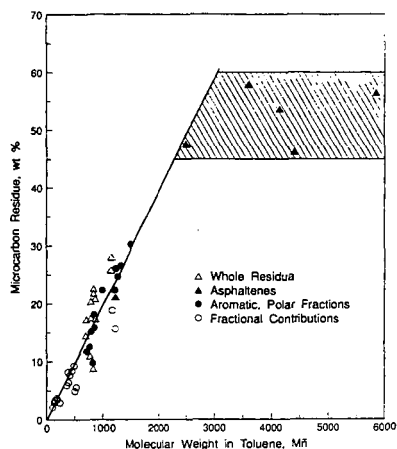

Figure 1. Microcarbon Residue vs. Molecular Weight for Residua Asphaltenes, Chromatographic Fractions, and Fractional Contributions in Toluene.

In an unrelated study (16,17) Athabasca bitumen pentane asphaltenes were separated into four ion exchange chromatography fractions. These materials were fully soluble in pyridine. The MCR values for these materials are plotted against their weights in pyridine. For reference, the toluene correlation line developed in Figure 1 is shown in Figure 2, and also the MCR value of the whole asphaltenes plotted against the molecular weight in benzene, which is essentially the same value one would expect in toluene.
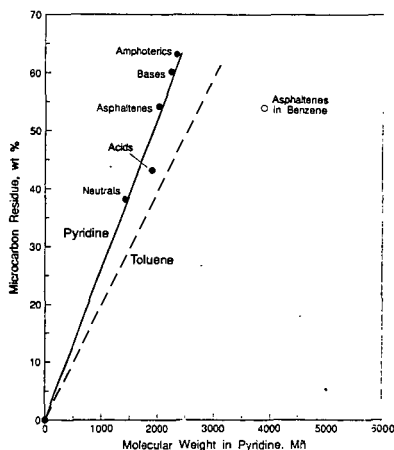

Figure 2. Microcarbon Residue vs. Molecular Weight for Athabasca Asphaltenes and Asphaltene IEC Fractions in Pyridine

The MCR values decrease in the order amphoteric, base, whole asphaltenes, acid, and polar

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neutral fractions (16). The point for the original asphaltene molecular weight in benzene falls far to the right of the line, with a MCR value of 54.0 and a molecular weight value of 3,890 Daltons. The pyridine molecular weight for the whole asphaltene is 2,018 Daltons (17). The equation for the pyridine line was calculated by including the origin point (0,0) to obtain a slope of 0.0262 and an intercept of -0.46, with a correlation coefficient of 0.990. The slope of the toluene line (0.0198) is smaller than the slope of the pyridine line, which is due to less association in pyridine.

The correlation lines can be used as a tool to gauge association. For example, to bring the asphaltene with the highest apparent molecular weight of 5,850 Daltons to the toluene line in Figure 1 without changing its MCR value would require a molecular weight of about 2,950 Daltons. Thus, it appears that the association tendency for this material is $5,850 â 2,950 = 2.0$ units average in an associative complex in toluene solution. Using the pyridine line in Figure 2, the same MCR value yields a molecular weight value of 2,250, or 2.6 average units in an associative complex in toluene. The associative forming tendencies do not appear to have a direct affect on MCR values. This is suggested by the flattening of the correlation above a molecular weight of 3,000 Daltons in toluene (Figure 1), which appears to be due mainly to associative effects. The associations are broken up by the severe heating conditions involved in carbon residue formation.

A correlation which is more useful for the highly associated species is between carbon residue and H/C atomic ratios (Figure 3). Figure 3 includes points for all the materials in Figures 1 and 2. The correlation coefficient is 0.975, for 33 points with a slope and intercept of -105 and 173, respectively. Two points lying far off the line, correspond to a very waxy residuum and its wax-containing asphaltenes and these were not included in the calculation. The point of intersection at MCR = 0 wt.% occurs at a H/C ratio of 1.65. This implies that for residua constituents that there will be no carbon residue contribution for most species with H/C atomic ratiosgreaterthanabout 1.65.
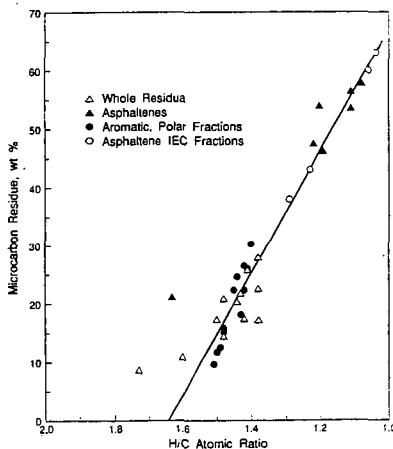

Figure 3. Microcarbon Residue vs. H/C Atomic Ratio for Residua, Asphaltenes, and Chromatographic Fractions

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